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Cole–Davidson dynamics of simple chain models

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Rotational relaxation functions of the end-to-end vector of short, freely jointed and freely rotating chains were determined from molecular dynamics simulations. The associated response functions were obtained from the one-sided Fourier transform of the relaxation functions. The Cole–Davidson function was used to fit the response functions with extensive use being made of Cole–Cole plots in the fitting procedure. For the systems studied, the Cole–Davidson function provided remarkably accurate fits [as compared to the transform of the Kohlrausch–Williams–Watts (KWW) function]. The only appreciable deviations from the simulation results were in the high frequency limit and were due to ballistic or free rotation effects. The accuracy of the Cole–Davidson function appears to be the result of the transition in the time domain from stretched exponential behavior at intermediate time to single exponential behavior at long time. Such a transition can be explained in terms of a distribution of relaxation times with a well-defined longest relaxation time. Since the Cole–Davidson distribution has a sharp cutoff in relaxation time (while the KWW function does not), it makes sense that the Cole–Davidson would provide a better frequency-domain description of the associated response function than the KWW function does. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3050105]

I. INTRODUCTION

A common measure of rheological complexity employed in simulation studies of chain molecules is the shape of the rotational relaxation function of the molecular end-to-end vector. Previously,[1,2] we have studied this function in considerable detail in the time domain and, here, we examine the associated response function in the frequency domain. These two quantities mimic the two major classes of experimental investigations of liquid dynamics, and the relationship between the functional forms in the two domains has been of long standing interest. The relationship between the most common time-domain form of the relaxation function [the Kohlrausch–Williams–Watts (KWW) function] and the most common frequency-domain form of the response function [the Cole–Davidson (CD) function] was investigated nearly 30 years ago by Lindsey and Patterson.[3] In the present work, it is demonstrated that the applicability of the CD function to simulation results is good and that the simulation relaxation functions are not strictly of the KWW form.

The molecular models studied are of the tangent site, bead-spring type. The chains are ten sites long with some systems having no bond angle restrictions [freely jointed (FJ) chains] and some having bond angles restricted to 120° [freely rotating (FR) chains]. These are standard models that have been shown to possess dynamical features similar to those of small molecular glass formers. Details have been reported elsewhere[1,2,4–7] and are summarized in Sec. II.

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The measure of rotational relaxation employed in the present work[1,2] is the second Legendre polynomial of the chain end-to-end vector

$$E(t) = \tfrac{3}{2}\left(\langle[\underline{e}(t)\cdot\underline{e}(0)]^2\rangle - \tfrac{1}{3}\right), \tag{1.1}$$

where the angle brackets denote ensemble average and $\underline{e}(t)$ is the unit vector along the end-to-end vector at a time t. The nature of the average ensures that $E(0)$ equals 1 and that the long time limit of $E(t)$ is 0. A typical example is plotted in Fig. 1(a). An exponential (or Debye) function[8] is also plotted in the figure as $\beta=1$, and it can be seen that this does not fit the $E(t)$ very well.

A better fit is given by the KWW function[9]

$$E_{\mathrm{KWW}}(t) = e^{-[(t/\tau_{\mathrm{KWW}})^{\beta_{\mathrm{KWW}}}]}, \tag{1.2}$$

where τ_{KWW} is a relaxation time, β_{KWW} is the "stretching exponent," and the value of β_{KWW} is between 0 and 1. In Fig. 1(a), KWW functions with β_{KWW} equal to 0.5 and 0.75 are shown. For the selected simulation result, KWW with β_{KWW} approximately equal to 0.75 provides a better fit than the Debye ($\beta=1$) function; however, it is still of low fidelity.

A functional form that does describe the simulation results to a high degree of accuracy is the modified-KWW (mKWW) (Ref. 10) function. This is defined in a piecewise manner,

$$E_{\mathrm{mKWW}}(t) = E_{\mathrm{ballistic}}(t) \quad \text{for } t < t_B,$$

$$E_{\mathrm{mKWW}}(t) = Ze^{-[(t/\tau_{\mathrm{mKWW}})^{\beta_{\mathrm{mKWW}}}]} \quad \text{for } t_B < t < t_T, \tag{1.3}$$

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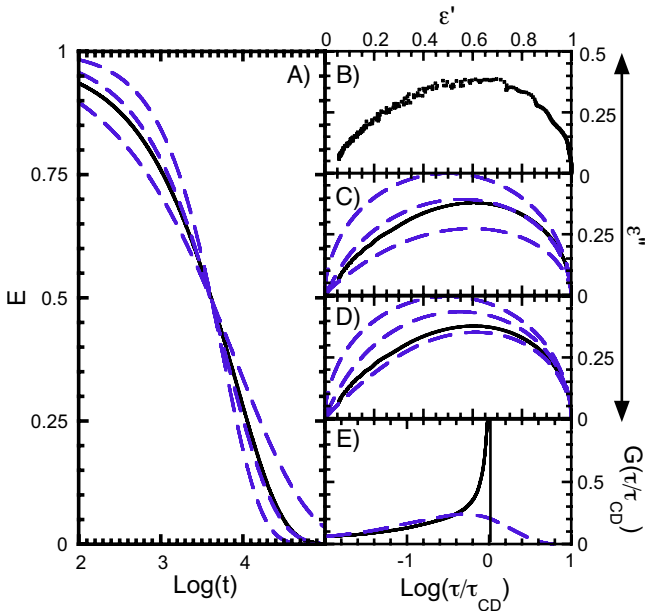

FIG. 1. (Color online) (a) $E(t)$ Solid line: Simulation FR-R ($T=1.6$, $\rho=1.06$, and $\eta=0.551$). Dashed lines: KWW (at low t, top curve, $\beta=1$; middle, $\beta=0.75$; bottom, $\beta=0.5$). (b) CC plot of the transform of $E(t)$ without smoothing. (c) CC plot of $E(t)$ smoothed with a single exponential patch (solid line) with KWW curves (top dashed line, $\beta=1$; middle, $\beta=0.75$; bottom, $\beta=0.5$). (d) Same as (c) but with CD curves (top dashed line, $\beta=1$; middle, $\beta=0.75$; bottom, $\beta=0.5$). (e) Relaxation time distribution function (solid curve: CD with $\beta=0.37$, $\tau=1$; dashed curve: KWW with $\beta=0.5$, $\tau=0.25$).

$$E_{\mathrm{mKWW}}(t) = Z_{\mathrm{tail}} e^{-(t/\tau_{\mathrm{tail}})} \quad \text{for} \quad t_T < t,$$

where the short time ballistic (or inertial) region is fit in a variety of manners (a Debye function being a common choice). The relatively large number of parameters (Z, τ_{mKWW}, β_{mKWW}, Z_{tail}, τ_{tail}, t_B, and t_T) makes this function challenging to fit in a consistent manner even when ignoring the detailed form of the ballistic region. For the systems studied here, fitting with the mKWW function was treated in previous papers.[1,2] The parameters in the intermediate time regime are not identical to the parameters of a full KWW functional fit. Indeed, depending on the fitting procedure, a range of KWW parameters can be found.

Because of these difficulties in performing a KWW fit, a common alternate path[3,11] to fitting relaxation functions is the generalized Maxwell model where an infinite number of spring-dashpot units are coupled in parallel

$$E(t) = \int_{-\infty}^{\infty} G(\tau) e^{-(t/\tau)} d\ln(\tau), \tag{1.4}$$

and where the distribution of relaxation times $G(\tau)$ is the fitting parameter. As might be expected, the consistent treatment of $G(\tau)$ is challenging in its own right, in most cases requiring that additional smoothness conditions be imposed in order for a unique solution to exist.

Many experimental determinations of relaxation functions are more conveniently performed and analyzed in terms of frequency. Consequently, it is common to transform between the time and frequency domain. In the case of $E(t)$, this transform[3] is

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty e^{-i\omega t} \left(-\frac{d}{dt} E(t) \right) dt, \tag{1.5}$$

where $\varepsilon^*(\omega)$ is the complex response function, ω is the frequency, ε_∞ is the high frequency limit, and ε_0 is the low frequency limit. For the cases that we will consider, ε_∞ is zero and ε_0 is unity. The complex modulus expressed in terms of the storage modulus $\varepsilon'(\omega)$ and the loss modulus $\varepsilon''(\omega)$ is $\varepsilon^*(\omega)=\varepsilon'(\omega)+i\varepsilon''(\omega)$, where $i=\sqrt{-1}$.

The transform to the frequency domain of numerical data has difficulties because of noise in the long time tail. In Fig. 1(b), the simulation results in Fig. 1(a) have been transformed without smoothing the data. The loss has been plotted against storage modulus in Cole–Cole (CC) form.[12] The roughness of the curve is the result of noise at long times. In Fig. 1(c), the mKWW fit of the tail region was used in the transform. This generates a much smoother frequency-domain representation. Also in Fig. 1(c), the transforms of the (pure) KWW curves in Fig. 1(a) are shown. Here too, it is evident that the KWW function, although better than the Debye function, does not capture the detailed shape of the simulation results. CC plots are particularly useful when assessing the degree to which time-temperature superposition holds. Time (or frequency) enters only indirectly in the plot as the distance along the curve with low frequency results to the right. Consequently, if time-temperature superposition holds, identical CC plots should be found at all temperatures and, thus, such a plot is a useful tool in assessing the degree of rheological complexity.[12]

For frequency domain studies, it is convenient to use a fitting function explicitly in terms of frequency. The most common of these is the CD function[13]

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \left(\frac{1}{1 + i\omega\tau_{\mathrm{CD}}} \right)^{\beta_{\mathrm{CD}}}, \tag{1.6}$$

where $0 < \beta_{\mathrm{CD}} \leq 1$. The storage and loss moduli can be expressed[14] in analytic form as

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \cos(\beta_{\mathrm{CD}}\theta)\cos^{\beta_{\mathrm{CD}}}(\theta) - i\sin(\beta_{\mathrm{CD}}\theta)\cos^{\beta_{\mathrm{CD}}}(\theta), \tag{1.7}$$

where $\theta=\arctan(\omega\tau_{\mathrm{CD}})$. The CD function is an attractive choice as a fitting function because of its small number of parameters and simple analytic from. Of course, these parameters are not necessarily identical to the similarly named ones in the KWW function.

In Fig. 1(d), the CC plot of the simulation example is compared to the CD function for β_{CD} of 0.5, 0.75, and 1 (where $\beta_{\mathrm{CD}}=1$ is the Debye function). Even without a detailed analysis, it can be seen that a CD function with a β_{CD} a little more than 0.5 would fit the simulation results to a high degree of accuracy. This is not a universal result. A similar comparison[3] of KWW and CD for a dielectric study of poly(propylene glycol) concludes that KWW provides the better functional fit. One of the primary points of the current paper is that for the small molecular systems studied, CD is more accurate than KWW and is comparable to the mKWW fit. The difference in the poly(propylene glycol) case may

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result from the range of β fitted ($\beta_{CD} \sim 0.35$ in one case and ~ 0.6 in the other), from molecular weight differences, or from subtle distinctions between dielectric testing and the rotational relaxation tracked in simulation.

From a more mathematical perspective, it appears that CD provides a better fit to simulation because it has a well-defined longest relaxation time. In Fig. 1(e), $G(\tau)$ for comparable KWW and CD functions are shown. The peak at $\tau = \tau_{CD}$ provides a clear cutoff value, while the KWW distribution smoothly decays and does not have a well-defined longest relaxation time. Moreover, the CD $G(\tau)$ has an analytic form[3,15]

$$G_{CD}(\tau) = \frac{\sin(\pi\beta_{CD})}{\pi}\left(\frac{\tau}{\tau_{CD}-\tau}\right)^{\beta_{CD}} \quad \tau < \tau_{CD},$$
$$G_{CD}(\tau) = 0 \quad \tau_{CD} < \tau, \tag{1.8}$$

which makes the calculation of $E_{CD}(t)$ straightforward through Eq. (1.4). Conversely, for cases lacking an exponential tail region (i.e., lacking a well-defined longest relaxation time), one would not expect the CD to fit as well as KWW.

In the remainder of the paper, we elaborate on the following themes. The CD function is shown to fit the simulation results to a high degree of accuracy, particularly at low frequencies, while deviations at high frequency can be understood in terms of the ballistic region of $E(t)$. The applicability of time-temperature superposition is shown to depend, to a degree, on the presentation of $\varepsilon''(\omega)$ data with log-log plots tending to concur and linear-log plots to differ with time-temperature superposition. When plotted as a function of packing fraction, the CD parameters show the same trends as seen in those of the mKWW function. In particular, β_{CD} and β_{mKWW} both decrease with increasing packing fraction indicating a broadening distribution of relaxation times as the glass transition is approached. Finally, the relationship previously proposed[3] between CD and (pure) KWW parameters approximately holds for the relationship between CD and mKWW parameters.

In particular, in Sec. II, simulation methods are briefly discussed and the reader is referred to previous papers for additional details. Pertinent results from our previous papers are reviewed, and the mechanics of the frequency domain analysis are presented in some detail. In Sec. III, our results are presented along with a cursory comparison to results of other researchers. In Sec. IV, the observations in the literature that help place our work in context are discussed in some depth. We conclude in Sec. V with general comments on the significance of our study.

II. BACKGROUND AND METHODS

Liquid relaxation occurs across many time and length scales. Small molecular units flip, entire molecules rotate, and clusters of molecules move cooperatively. Each type of motion has its own signature, and these overlap in ways difficult to decipher. The most interesting of these is cooperative motion. This grows in extent in the vicinity of the glass transition and is believed to be the cause of the dominant features of the glass transition such as the slowing down of relaxation times, the divergence of viscosity, the broadening of the distribution of relaxation times, the breakdown of time-temperature superposition, and, in general, the display of rheological complexity.

Simple molecular models reduce the number of noncooperative modes and permit longer time scales to be investigated. Consequently, the analysis of such systems is easier, and the onset of rheological complexity, more clearly observed. The models we study are based on tangent bead-spring chains of ten sites. The sites interact through Lennard-Jones 6–12 potentials

$$U_{LJ}(r) = 4\xi\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{2.1}$$

where r is the site-site separation, σ is the length scale, and ξ is the well depth. In addition, bonded sites interact through a finitely extensible nonlinear elastic potential.[16] The simulations are performed with LAMMPS molecular dynamics software[17] and contain 80 chains and five single beads. This is a standard model, which we denote as attractive FJ (FJ-A).

The FJ-A system is modified in two manners. First, we truncate the Lennard-Jones potential at the minimum and add ξ to investigate repulsive interactions. This allows systems with longer relaxation times to be run and avoids complications associated with the liquid-gas transition. These are repulsive FJ (FJ-R). Second, we fix the bond angle of the chains at 120°. These are referred to as FR and both attractive (FR-A) and repulsive (FR-R) cases are considered.

These models are sufficiently simple that a straightforward definition of the packing fraction η is found[4–6] to be a useful measure of the distance to the glass transition

$$\eta = \frac{\pi}{6}\rho d^3, \tag{2.2}$$

where ρ is the site density. For the repulsive systems, the effective hard-site diameter d is given by

$$d = \int_0^\infty \left|1 - \exp\left(-\frac{U_{rep}(r)}{kT}\right)\right| dr, \tag{2.3}$$

where $U_{rep}(r)$ is the repulsive part of the potential and k is the Boltzmann constant. Attractive systems have the further correction

$$\frac{d_A}{d_R} = \frac{r_A}{r_R}, \tag{2.4}$$

where d_A is the hard site diameter for the attractive system, d_R is the hard site diameter as calculated through Eq. (2.3), and r_A and r_R are the locations of the first peak in the pair correlation function for the equivalent attractive and repulsive systems found through simulation. Equivalent systems have the same temperature and density. Details of the calculation are reported in Refs. 1, 2, and 4–6.

In previous papers,[1,2,4–6] we have demonstrated that various dynamic quantities such as τ_{mKWW} and β_{mKWW} are single-valued functions of η. We employ η in a similar capacity for the analysis of the CD fitting of $E(t)$. In effect, this incorporates pressure as well as temperature into a measure of the distance to the glass transition $(\eta_0 - \eta)$, where η_0 is the

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packing fraction of the ideal glass transition. This is an approach similar to that of Roland *et al.*[18] where η would be proportional to $1/(\underline{V}T^{1/\gamma})$, $\underline{V}$ is the molar volume, and γ is a constant adjusted to collapse the data collected at different temperatures and pressures. The η for hard spheres is independent of temperature implying $\gamma=\infty$. For the FJ systems, it is found[6] for the FJ-A systems $\gamma\sim 8.0$ and for the FJ-R systems $\gamma\sim 12.0$. These values correspond to strong liquids (see Figs. 16 and 22 of Ref. 18).

The fitting of the mKWW function to time-dependent data is nontrivial. A consistent methodology for performing such fits is described in detail in a previous work.[1] It was found that the intermediate time region of KWW behavior could be determined by taking advantage of two conversions of the data. Under the assumption that the end-to-end function is described by a stretched exponential (Eq. (1.2)) the following relationships hold

$$\ln[-\ln[E_{\mathrm{mKWW}}(t)]] = \beta \ln(t/\tau_{\mathrm{mKWW}}) + \ln\left|1 - \frac{\ln(Z)}{(t/\tau_{\mathrm{mKWW}})^{\beta_{\mathrm{mKWW}}}}\right|, \quad (2.5)$$

$$\ln\left[-\frac{d\ln(E_{\mathrm{mKWW}}(t))}{d\ln(t)}\right] = \beta \ln(t/\tau_{\mathrm{mKWW}}) + \ln(\beta_{\mathrm{mKWW}}). \quad (2.6)$$

Consequently, the two conversions are related in the following manner:

$$\ln[-\ln[E_{\mathrm{mKWW}}(t)]] = \ln\left[-\frac{d\ln(E_{\mathrm{mKWW}}(t))}{d\ln(t)}\right] - \ln(\beta_{\mathrm{mKWW}}) + \ln\left|1 - \frac{\ln(Z)}{(t/\tau_{\mathrm{mKWW}})^{\beta_{\mathrm{mKWW}}}}\right|. \quad (2.7)$$

For sufficiently large t the last term is negligible, and, as a result, the cross plot of the two conversions has a slope of one and an intercept of $-\ln(\beta_{\mathrm{mKWW}})$ in the KWW region. This methodology is reasonably robust, and, when applied to simulation data, produces results in line with experimental trends.[1] For times longer than the KWW region, it was necessary to "patch" on a single exponential tail, while for small times, agreement with the KWW function was not expected. Consequently, accurate fitting in the time domain requires seven parameters: three parameters for the KWW region, two parameters for the single exponential tail region, and two parameters for the location of the crossover times from ballistic to KWW and from KWW to single exponential tail. Details are reported in Ref. 1.

In addition to fitting in the time domain, the transformation of the relaxation functions to the frequency range is also of interest. The noise in the transform to the frequency domain is reduced in two manners. First, advantage is taken of the well-known property[19] of Laplace transforms

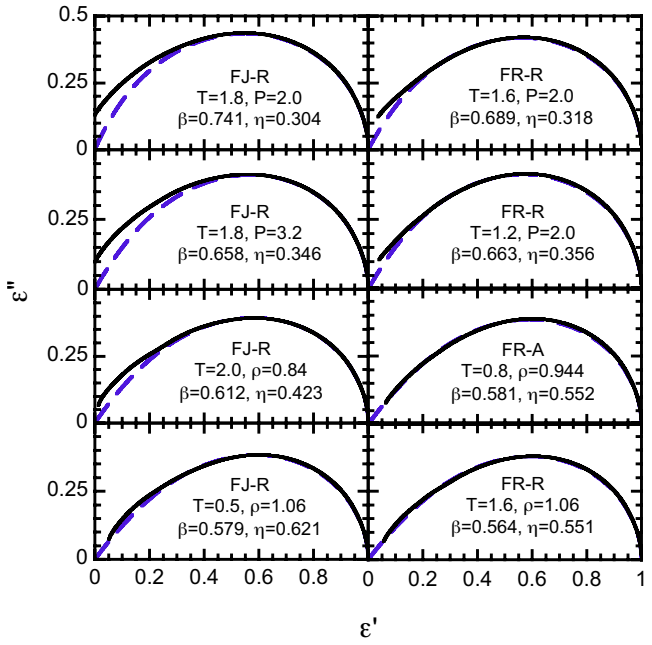

FIG. 2. (Color online) CC plots for a selection of systems as denoted. Solid lines are simulation results. Dashed lines are CD fits with indicated parameters. T has units of ξ/k and ρ has units of $1/\sigma^3$.

$$L\left(\frac{d}{dt}\phi(t)\right) = i\omega L(\phi(t)) - \phi(0), \quad (2.8)$$

where L denotes the Laplace transform. This eliminates the introduction of noise from the numerical derivative. Second, the long time region of the end-to-end function is replaced with the single exponential function found to describe this region. These smoothing procedures reduce the wild oscillations while retaining the fundamental character of the curve, as shown in Fig. 1. These transforms were calculated for numerous cases, and selected CC plots are shown in Fig. 2.

There are a number of physical limits on the shape of the CC plot.[20] First, the Debye semicircle is an upper bound except at high frequencies. Second, the slope at the low frequency (right) intercept with the ε'-axis is vertical. Third, the slope at the high frequency (left) intercept is zero and approaches from the left.

All of the functional forms considered here violate the last of these. The Debye function has a vertical slope at the high frequency intercept. The CD function has a nonzero slope and approaches from the right. The KWW function (when transformed to the frequency domain) has a high frequency limit similar to the CD function. This effect is a consequence of the particulate nature of the material.[20] At short time (high frequency), particles behave ballistically with the consequence that the relaxation function has zero slope at $t=0$. The Debye, CD, and KWW functions are incorrect in this limit. Consequently, the disagreement seen in Fig. 2 between the CD function and simulation is expected and reasonable.

The systems in Fig. 2 are arranged from low to high η. The β_{CD} parameter is seen to decrease with increasing η. More interesting is the increased agreement between simulation and CD fit. Since low η systems would be expected to have a more pronounced free rotation or ballistic region, it is

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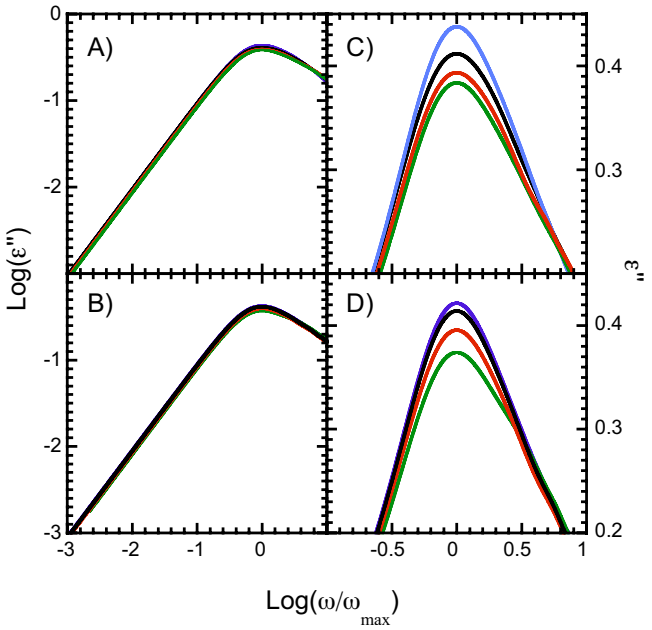

FIG. 3. (Color online) Loss modulus vs ω shifted by ω at maximum. Panels (a) and (c) are FJ; (b) and (d) are FR. Same data plotted in left- and right-hand plots. In (c) from top to bottom are (FJ-R, $T=1.8$, $P=2.0$, $\eta=0.304$), (FJ-R, $T=1.8$, $P=3.2$, $\eta=0.346$), (FJ-R, $T=2.0$, $\rho=0.84$, $\eta=0.423$), and (FJ-R, $T=0.5$, $\rho=1.06$, $\eta=0.621$). In (d) from top to bottom are (FR-R, $T=1.6$, $P=2.0$, $\eta=0.318$), (FR-R, $T=1.2$, $P=2.0$, $\eta=0.356$), (FR-R, $T=2.0$, $\rho=0.944$, $\eta=0.477$), and (FR-A, $T=1.6$, $\rho=1.06$, $\eta=0.563$).

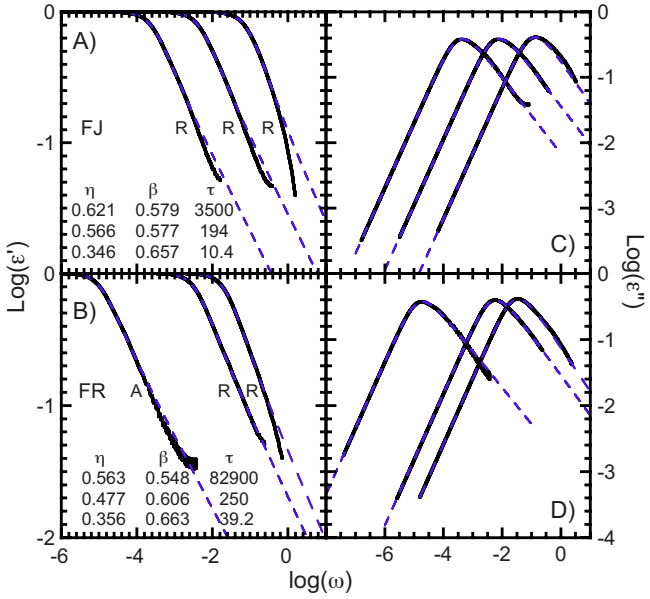

FIG. 4. (Color online) CD fits for $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$. (a) and (b) are storage moduli $\varepsilon'(\omega)$. (c) and (d) are loss moduli $\varepsilon''(\omega)$. (a) and (c) are FJ. (b) and (d) are FR. In (a) and (c) from left to right: ($T=0.5$, $\rho=1.06$), ($T=1.0$, $\rho=1.033$), and ($T=1.8$, $P=3.2$). In (b) and (d) from left to right: ($T=1.6$, $\rho=1.06$), ($T=2.0$, $\rho=0.944$), and ($T=1.2$, $P=2.0$). Additional information on plot: top to bottom corresponds to left to right: R=repulsive and A=attractive.

reasonable that the corresponding region of disagreement with the CD function would also be more pronounced. In addition, FJ systems would be expected to have a larger ballistic region than FR systems, and the closer agreement for the FR systems is consistent with this.

The variation in β_{CD} indicates rheological complexity. However, care must be taken. This variation must be more than the uncertainty in the fitting procedure. The consistent decrease in β_{CD} with increasing η is reassuring. On the other hand, this same information, plotted differently, can lead one to conclude that the systems are simple rather than complex. Figure 3 is an illustration of this. Examples of the loss modulus ε'' are given for selected FJ and FR systems with the frequency reduced by ω_{max}. When ε'' is plotted on a log-log scale, as in Figs. 3(a) and 3(b) (and as is common experimental practice when several decades of data are available), the differences between the curves are minimized. This implies that time-temperature superposition is obeyed and that the system is rheologically simple. However, linear-log plots of the same data show that the shape of the peak does, indeed, vary with state point [Figs. 3(c) and 3(d)]. Clearly, discretion is necessary when using the terms simple and complex.

In Fig. 4, the storage and loss moduli are shown as a function of frequency. The CD function is seen to fit the simulation results to a high degree of accuracy. The differences at high frequency are, for the most part, due to errors in the transform; however, because of the ballistic region (discussed above), ε' is expected to be negative at sufficiently high frequency and the logarithm would diverge. This effect is clearer in the CC plots.

III. RESULTS

It is intriguing that the CD function fits the simulation results so well. However, it is desirable to demonstrate that the parameters β_{CD} and τ_{CD} vary systematically as the glass transition is approached. In this section, we view the results from numerous simulations in terms of the packing fraction. From this we draw conclusions about the degree of rheological complexity in the systems and about the relationship between the CD and the mKWW parameters.

The procedures outlined in Sec. II to transform the time relaxation functions to the frequency domain were applied to the data set previously analyzed[1] with a mKWW procedure. The reported values of β_{CD} and τ_{CD} are the averages of those obtained from fitting the real and imaginary parts. Except at high frequencies, the data are well described by the CD function, and, in terms of the CC plot, discrepancies do not appear until well to the left (high ω side) of the maximum. This permits the CD function to be fit without the need to "clip" the data at low frequency (as is necessary with mKWW fits). Since the simulation results have a long time limit of single exponential behavior, the low frequency accuracy of the CD function is the consequence of its well-defined longest relaxation time.

For the systems investigated here, the behavior of β_{CD} with respect to η closely mirrors that of β_{mKWW} [Figs. 5(a) and 5(b)]. Both methods result in the collapse of β to a single-valued function of packing fraction. The β decrease with increasing η as is typically the case as the glass transition is approached. The FJ systems have a pronounced plateau region at large η where time-temperature superposition would (approximately) be obeyed. The FR systems lack this plateau and would be rheologically complex over the entire range of η studied.

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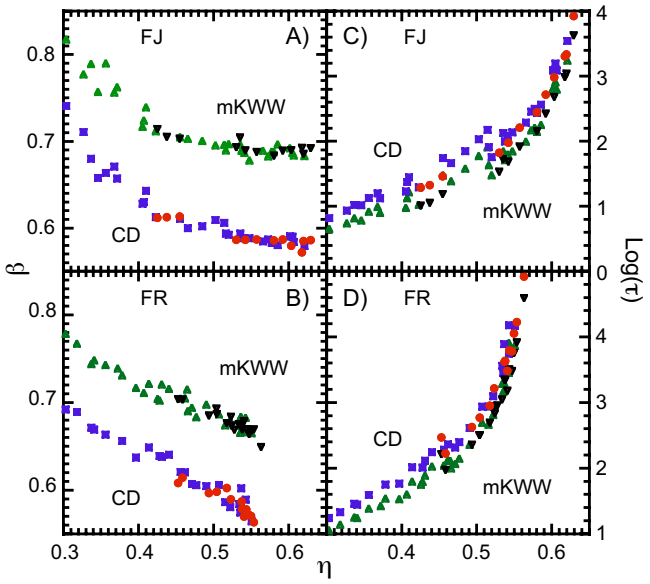

FIG. 5. (Color online) Stretching parameter β and relaxation time τ as a function of packing fraction η. (a) and (c) for FJ systems. (b) and (c) for FR systems. Results for both CD (squares, circles) and mKWW (triangles, inverted triangles) fits. Both repulsive (triangles, squares) and attractive (inverted triangles, circles) results are reported.

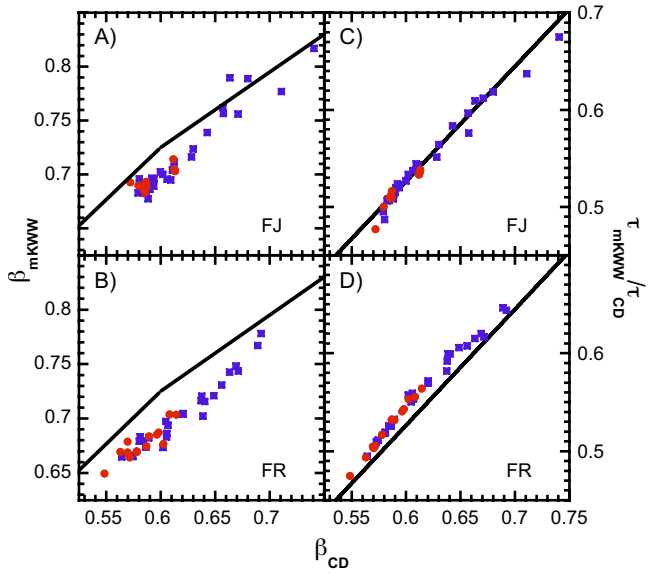

FIG. 6. (Color online) Correlation between parameters for two fitting procedures: mKWW and CD. Stretching parameter β_{mKWW} and ratio of characteristic times τ_{mKWW}/τ_{CD} as a function of β_{CD}. (a) and (c) for FJ systems. (b) and (c) for FR systems. Both repulsive (squares) and attractive (circles) results are reported. Lines denote Lindsey–Patterson relationships between CD and KWW.

The CD and KWW values of β should not be identical. The two functions are not equivalent. The transform of the (pure) KWW function into the frequency domain does not lead to the CD function. However, both β are restricted to values between 0 and 1, and, in both cases, a decrease in β increases the non-Debye broadening of the peak in the loss modulus. Indeed, the width at half max of the loss peak has much of the information content of β since peak width increases as β decreases.

The CD and mKWW β differ by a value of roughly 0.1. More careful analysis shows the relationship to be linear [Figs. 6(a) and 6(b)] for both FR and FJ systems. The relationships are

$$\beta_{mKWW} = 0.747\beta_{CD} + 0.253 \tag{3.1}$$

for FJ systems and

$$\beta_{mKWW} = 0.777\beta_{CD} + 0.222 \tag{3.2}$$

for FR systems. The fits were regularized by taking advantage of the fact that for $\beta_{CD}=1$ the curve is a Debye function and therefore it is required that $\beta_{mKWW}=1$ as well. These relationships differ from the one found by Lindsey and Patterson[3] [Figs. 6(a) and 6(b)] in their CD fits of the transform of a pure KWW function

$$\begin{aligned} &\beta_{KWW} = 0.970\beta_{CD} + 0.144, \quad 0.2 \le \beta_{CD} \le 0.6, \\ &\beta_{KWW} = 0.683\beta_{CD} + 0.316, \quad 0.6 \le \beta_{CD} \le 1.0. \end{aligned} \tag{3.3}$$

This difference between our analysis of simulation results and the Lindsey–Patterson analysis of the (pure) KWW function reflects that the simulation relaxation functions are not globally described by the KWW function.

A similar correlation between the mKWW and CD functions was found for the decay constants τ_{mKWW} and τ_{CD} [Figs. 5(c) and 5(d)]. The relationships between τ_{mKWW} and τ_{CD} are

$$\tau_{mKWW} = \tau_{CD}(1.188\beta_{CD} - 0.188) \quad \text{(FJ)}, \tag{3.4}$$

$$\tau_{mKWW} = \tau_{CD}(1.141\beta_{CD} - 0.141) \quad \text{(FR)}. \tag{3.5}$$

Again, it was required that both mKWW and CD fits approach the Debye limit at small η (i.e., when $\beta_{CD}=\beta_{mKWW}=1$, it is required that $\tau_{CD}=\tau_{mKWW}$). The Lindsey–Patterson[3] prediction for the relaxation time of the (pure) KWW function is

$$\tau_{KWW} = \tau_{CD}(1.184\beta_{CD} - 0.184) \tag{3.6}$$

and is in good agreement with the relationship between mKWW and CD for the FJ systems but less so for the FR systems.

Comparison with Leporini and co-workers[21,22] provides a check on our results. They have studied the rotational dynamics of both the two-site and ten-site versions of our FJ-R systems. The β_{CD} can be extracted from the high frequency exponent of the loss modulus of ten-site chains for pressure $(P)=2.0$ [see Fig. 15(b) of Ref. 22]. β_{CD} is roughly 0.7, which is in agreement with our results at that pressure and over the temperature range studied (and β_{KWW} is reported to be 0.8). The β_{KWW} found from the diatomic version was considerably smaller[21] with a value of 0.6. Additional detail on the rotational relaxation of the FJ model can be found in Ref. 23.

IV. DISCUSSION

The choice of best fitting function in the frequency domain depends on molecular detail. For the simple molecular

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models studied here, the CD function works extremely well as does the mKWW while the unmodified KWW function gives only a poor fit. However, experiments on small molecules often are best fit with the KWW function, large (although not polymeric) molecules often are best fit with the CD function, and polymeric molecules often are best fit with the Havriliak–Negami (HN) (Ref. 24) function. There are many exceptions. Niss *et al.*[25] provided an excellent discussion of the relative merits of the different fitting functions. Figure B.1 of Ref. 25 compares a variety of fits of the loss modulus for *m*-toluidine ($\beta_{\mathrm{KWW}}=0.57$, $\beta_{\mathrm{CD}}=0.42$) with the CD fit being clearly superior to the KWW fit. Of course, over narrow frequency ranges, it can be difficult to distinguish one functional form from another.[26]

The KWW function is the most commonly used simple form. In the time domain, the KWW function is ubiquitous, although, in many cases, the KWW is modified to obtain accurate fits. In the frequency domain, there is a larger selection of fitting functions; even so, the frequency transform of the KWW function can still be the best fit. A well-known advocacy of the KWW function is the Lindsey and Patterson's[3] fit of poly(propylene glycol) discussed above. Moreover, the KWW function can be derived from a generalized diffusion equation[27] and this makes the KWW seem more physically based than other functions. From this perspective, deviations from KWW in the frequency domain are assumed to be the result of non-α relaxation processes. Fitting involves subtracting the KWW transform from the experimental data, assuming the reside is a β-process, and fitting this separately often with the CC function,

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}=\frac{1}{1+(i\omega\tau)^\alpha}. \tag{4.1}$$

Examples are given in Refs. 28 and 29.

In the frequency domain, the advantages of the KWW over the Debye function are easily seen in the log-log plot of the loss modulus versus frequency [as in Figs. 4(c) and 4(d)]. The linear behavior at high and low frequencies indicates two power-law regimes. The Debye function has a low frequency exponent of 1 and a high frequency exponent of −1. This is only rarely seen in experiments. The KWW function has a high frequency exponent of $-\beta_{\mathrm{KWW}}$ which can be adjusted to fit the experiment (its low frequency exponent of 1 is often in good agreement). Unfortunately, the β_{KWW} needed to fit the peak is not necessarily the same as is needed to fit the power-law region.[30] This inconsistency in β_{KWW} is also expressed in a poor fit in the CC plot [as seen in Fig. 1(c)].

The KWW does not necessarily capture the time-domain behavior. See, for instance, the work of Bovelli *et al.*[31] where the rotational relaxation of two rigid glass formers was studied with depolarized photon correlation spectroscopy. The relaxation function of the small molecule glass former is found to accurately be described by the KWW function; however, the larger molecule is found to deviate from KWW at large time in a manner similar to that seen in our simulation studies. When KWW does fit the data well, its transform to frequency space is not convenient. Ferguson *et al.*[32] provided a good discussion of the intricacies of the transform as well as showed that KWW is a good description for poly(vinyl acetate) and poly(isobutylene). Also see examples in Refs. 33 and 34.

In some ways, the CD and KWW functions are similar to each other. The CD function also has a low frequency exponent of 1 and an adjustable high frequency power law of $-\beta_{\mathrm{CD}}$. However, for the systems in our study, the β_{CD} needed to fit the peak and power-law regions are identical. A wide range of experimental results have been fit with the CD function. In particular,[35] "most systems with strong or intermediate fragility are well accounted for by the CD function." The fragility *m* defined as $d\log(\tau)/d(T_g/T)$ evaluated at $T=T_g$ is roughly related to β_{KWW} through[35] $\beta_{\mathrm{KWW}}=0.81-m/278$, where T_g is the experimental glass transition temperature. Consequently, both FJ and FR systems have fragilities of about 30, which implies that they are relatively strong liquids and that the CD function should work well, as it does. Additional discussions of the applicability of the CD function are given in Refs. 25 and 36–40. Examples of approximate mappings from CD to KWW are given in Refs. 3, 41, and 42.

In cases where the low frequency exponent is not 1, as is the case in some polymers, the HN function is often employed as

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}=\left[\frac{1}{1+(i\omega\tau)^\alpha}\right]^\gamma, \tag{4.2}$$

where the low frequency exponent is α and the high frequency exponent is $-\beta_{\mathrm{HN}}=-\alpha\gamma$. The HN distribution of relaxation times is similar to that of the CD with a relatively well-defined longest relaxation time. Typically only clear deviations from a low frequency exponent of 1 justify the additional parameter. Fragile glass formers such as sorbitol ($m=100$, $\alpha=0.8$) and toluene ($m=103$, $\alpha=0.7$) require[35] HN fitting for this reason. Kaminski *et al.*[33] provided a good example of combining HN and CC for a detailed fitting of ε'' as well as a demonstration of the difficulty that KWW can have in fitting the high frequency wing. Just as in the CD case, there have been a number of mappings from HN to KWW parameters.[25,38,43,44]

For any of the functional forms, the shape parameter β needs to remain constant in order for time-temperature superposition to be strictly obeyed. On the other hand, it is possible for variations in β to be the result of inconsistent curve fitting procedures instead of being a result of true rheological complexity. Indeed, it is not uncommon to be both able to construct a master curve and to find variations in β (with violations of master curve behavior being within the error bars).[45,46] From the experimental perspective this is clearly addressed by O'Connell and McKenna.[45,46] Referring to a stress relaxation study of polycarbonate, they find that "it is immediately clear that the KWW equation does not adequately describe relaxation over the whole range of data. This is surprising since the individual data sets at each temperature did appear to be described very well by KWW equations. So, although the KWW expression will fit the data over a short time scale (~4 decades), the deviation in the fits seems to show up when longer time scales are used (~7 decades)."

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Simulations also show this tendency. In addition to our previous papers,[1,2] Bordat *et al.*[47] commented on this for simulations of binary Lennard-Jones atomic glass formers. They find that "upon lowering the temperature from the normal liquid state, … the self-intermediate scattering functions progressively collapse onto an apparent master curve. However, a detailed view of this thick curve reveals that the different functions do not strictly superpose. Therefore, it is only approximately possible to extract a temperature independent stretched exponent β using a KWW fit of the master curve in a restricted temperature range."

Often, a high frequency exponent of −0.5 corresponds to master curve behavior[48] which implies a $\beta_{CD} \sim 0.5$. Wang and Richert[35] had a good discussion of this point. The systems they review only show a master curve behavior for β_{KWW} less than 0.57. This can be compared to our results in Fig. 5. The FJ systems permit master curve behavior for a $\beta_{KWW} \sim 0.7$ and a $\beta_{CD} \sim 0.58$ while the FR systems show little or no master curve behavior. We certainly agree with their comment that "the question of temperature invariant β should not be answered with a 'yes' or 'no' only."

One of the distinctive features of the CD function is its well-defined longest relaxation time. The CD-like distribution of relaxation times has been related to molecular motion in an interesting manner. The simple defect-diffusion model due to Glarum[49] assumes that in the uniform liquid, the molecules relax with a simple Debye function with relaxation time τ_D. In addition, there are mobile defects that diffuse through the liquid. In the presence of a defect, a molecule relaxes instantly. The solution of this model leads to a CD-like distribution of relaxation times. Modern extensions of this type of approach, known as dynamic facilitation models,[50] have led to elegant explanations of the glass transition in terms of trajectories in space time. In these models, the "defects" are envisioned as large regions of fast and slow dynamics (dynamic heterogeneity). Although most applications of these models have been to kinetically constrained spin models, relaxation functions of the KWW or CD form are predicted.[51,52]

V. CONCLUSIONS

In this study, we have continued our detailed characterization of the dynamics of simple molecular models. As in previous studies, it is seen that many of the complex dynamical features found in experimental systems are reproduced in the simple models. The simplicity of these models is of great benefit not only because of the lightened computational demands, but also because features in the dynamics can be more directly related to specific molecular details. In particular, the FR and FJ chains studied here have qualitatively different dynamics in spite of having similar molecular structures. The FJ systems are essentially rheologically simple (at least for large η) while the FR systems are rheologically complex over the entire range of η studied. Moreover, the simplicity of the models permits the packing fraction to be defined in a straightforward manner.

The ability of the CD function to describe the response function for the model systems was surprising. The KWW and CD functions are both two parameter functions and typically viewed as comparable. This was not the case in the current study. In order to achieve acceptable accuracy for the KWW function it was necessary to apply it in its modified form, which entailed the use of seven parameters. On the other hand, the CD function in its unaltered two-parameter form was as accurate as the seven-parameter mKWW.

The shape parameter β for CD is similar to that of mKWW. Although β_{CD} is smaller than β_{mKWW}, both are single-valued function of η and decrease as η increases. The relationships between mKWW and CD parameters are similar to those between pure KWW and CD parameters as reported by Lindsey and Patterson.[3]

The CC plots were useful in fitting the CD function to the simulation results. Because of the nature of the plot, only β_{CD} affects the shape of the plot (i.e., the shape is insensitive to τ_{CD}). It also clearly shows the deviations in the high frequency limit due to ballistic (or, more correctly, free rotational) motion. In the high frequency limit, the CC plot for a true molecular system must approach the origin from the left while the CD and KWW functions approach from the right. For small η the deviation from CD behavior is seen in the simulation results at high frequencies. Presumably, similar deviations exist at large η as well but are beyond the resolution of the simulations. Time-temperature superposition is expressed in a CC plot as the collapse onto a single curve without the necessity of shift factors. For our results, collapse does not happen for all η. This is seen in Fig. 2 where the CC plots deviate more and more from the Debye semicircle as η increases.

We believe that the higher accuracy of the CD function is the result of the sharp cutoff in the CD distribution of relaxation times. For times longer than the cutoff relaxation time τ_{CD}, the relaxation function in the time domain would quickly assume a Debye (or single exponential) form. Indeed, the modification of the KWW that was necessary for a good description of the simulations was of this nature. Beyond a certain time the KWW function was truncated and a single exponential tail was patched on. From the perspective of the underlying physics, this presence of a well-defined longest relaxation time can be explained in terms of a defect-diffusion (or dynamic facilitation) model where cooperative rearrangement induces a distribution of relaxation times.

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